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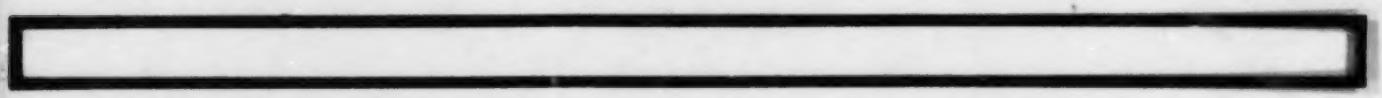

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RECOMMENDED PRACTICES FOR ON-LINE MEASUREMENT OF RESIDUAL CHLORINE IN WASTEWATERS

by

Gershon Kulin
Fluid Engineering Division
National Bureau of Standards
Washington, DC 20234

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Project Officer

Walter W. Schuk
Wastewater Research Division
Water Engineering Research Laboratory
Cincinnati, Ohio 45268

WATER ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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16. ABSTRACT

This document provides users with information that assists them in specifying, installing, calibrating, maintaining and monitoring the subsequent performance of on-line residual chlorine analyzers in wastewater treatment plants.

An on-line residual chlorine analyzer must have, among other characteristics: capability for continuous operation; a sampling system that assures a representative sample with the proper contact time; range of from 0-1 to 0-10 mg/L of chlorine residual depending upon the application; accuracy and precision within 3 percent and 1 percent of range, respectively; response time less than three minutes; and on-site readout and output capability for transmission to a controller and/or recorder.

Calibrations should be based on amperometric back titration and should be performed at frequencies that are based on documentation obtained during startup. Methods for developing this information and other procedures for measurement assurance are discussed. Recommended maintenance guidelines are given.

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water A , the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This document specifically provides improved guidelines for the selection, installation, calebration and maintenance of on-line residual chlorine analyzers used for monitoring and process control in wastewater treatment plants.

Francis T. Mayo, Director
Water Engineering Research Laboratory

ABSTRACT

This document provides users with information that assists them in specifying, installing, calibrating, maintaining and monitoring the subsequent performance of on-line residual chlorine analyzers in wastewater treatment plants.

An on-line residual chlorine analyzer must have, among other characteristics: capability for continuous operation; a sampling system that assures a representative sample with the proper contact time; range of from 0-1 to 0-10 mg/ℓ of chlorine residual depending upon the application; accuracy and precision within 3 percent and 1 percent of range, respectively; response time less than 3 minutes; and on-site readout and output capability for transmission to a controller and/or recorder.

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1. SCOPE

1.1 The equipment and procedures described in this document are intended for use in wastewater treatment plants, i.e., for residual chlorine measurements either for control purposes at various stages of the sewage treatment process or for monitoring the effluent.

1.2 The document includes:
- recommendations for preparing specifications for on-line residual chlorine analyzers, including sample lines and pumps; and
- recommendations for sampling and instrument calibration and for continued quality control of the analyzer-system performance.

2. DEFINITIONS

2.1 Accuracy -- The absolute nearness to a "true" value determined with an agreed-upon laboratory standard or procedure.

2.2 Amperometry -- Chemical analysis by measurement of electrical current flowing in an electrolyte solution. The current is a function of the concentration of a specific constituent in the sample.

2.3 Analyzer -- In this context, the residual chlorine analyzer is interpreted to include the entire instrument from sensor to readout and transmitter. A sampling system may or may not be included.

2.4 Breakpoint -- Process of adding chlorine to the wastewater being treated until the total chlorine residual has reached a minimum value (the breakpoint).

2.5 Combined residual chlorine -- Residual consisting of chlorine combined with ammonia nitrogen or nitrogenous compounds.

2.6 Contact time -- The amount of time the wastewater at a flow cross-section along the contact chamber has been in contact with chlorine.

2.7 Dechlorination -- The process of removing chlorine subsequent to treatment of wastewater and prior to its discharge. Sulfur dioxide is normally used for this purpose.

2.8 Free residual chlorine -- Residual consisting of hypochlorite ions (OCL^-), hypochlorous acid (HOCL), or their combinations.

2.9 Precision -- Agreement among a number of consecutive measurements of the same value of the input under the same operating conditions.

2.10 Range -- The region between the limits within which the concentration of residual chlorine is measured, received or transmitted, expressed by stating lower and upper range values. The meter range is the range that can be measured by the instrument, e.g., 0-10 mg/ℓ.

2.11 Response time -- The time required, after introduction of a step change from zero to a steady-state value of the parameter being measured, for an instrument to register a specified percentage of that step change.

2.12 Sampler -- A system made up of components such as piping, pump, flow-meter, etc., which conducts sample liquid to the sensor. It may be furnished as an integral part of the analyzer.

2.13 Sensitivity -- The minimum change of concentration detectable by the instrument.

2.14 Sensor -- In this context, the electrochemical cell which responds to the presence of residual chlorine.

3. INTRODUCTION

3.1 Purpose. The purpose of this document is to provide users with information that enables them to:
- select a suitable instrument (type and range) for making residual chlorine measurements as required for process control and/or effluent monitoring; and
- install, check, operate and maintain the system so that it will provide reliable and useful data on the concentration of residual chlorine.

3.2 Background.

3.2.1 Total residual chlorine may be defined as the amount of available chlorine (free and combined) present in water at any specified time. Except for cases where breakpoint chlorination is specified, the residual chlorine of most wastewater treatment plant effluents will be in the form of combined residual chlorine.

3.2.2 Monitoring of the level of residual chlorine is necessary to maintain chlorination levels above specified limits to insure adequate disinfection of the plant effluent and yet maintain chlorine discharge to receiving waters below prescribed limits.

3.2.3 Residual chlorine measurements are also made for control purposes during the chlorination process. In this case, the output of the analyzer may be used in a feedback mode as one of the parameters which adjust the rate at which chlorine is injected. An analyzer located at the effluent end of the process can serve in both monitoring and control roles.

3.2.4 The chlorine residual level required for adequate disinfection is dependent on such variables as pH, temperature, contact time, as well as the concentration of micro-organisms in the given waste. Note: Regulations governing permissible levels of residual chlorine in discharges vary among jurisdictions. Local regulatory agencies generally specify minimum total chlorine residuals, typically about 1 mg/ after 15 to 30 minutes contact. Upper limits as well are sometimes placed on the permissible level of residual chlorine at the discharge point in order to avoid toxicity in the receiving water. For example, California specifies a maximum chlorine residual of 0.1 mg/ in the undiluted effluent in selected areas (reference 8.4). Dechlorination may be necessary in such cases.

3.3 Principles of Operation.

3.3.1 Commercially available residual chlorine sensors that are suitable for use in sewage treatment plants operate on either electrochemical (polarographic and amperometric sensors) or colorimetric principles.

3.3.1.1 In polarographic sensors, chlorine species diffuse through a semipermeable membrane, which encapsulates a metal electrode, and are subsequently reduced to chloride at the electrode surface. The electrical current thus produced is determined by the rate of diffusion of chlorine species through the polymer membrane surrounding the microelectrode. The rate of diffusion, in turn, is a function of the concentration of chlorine species in the sample. It is clear that the integrity of the membrane is of vital importance, e.g., any defect will disrupt the characteristic of the sensor and will hence produce erroneous results. A minimum velocity of liquid flow past the membrane is usually specified.

3.3.1.2 In amperometric sensors, the flowing sample is mixed with a reagent solution which adjusts the sample to an appropriate pH value. Potassium iodide is also added when total residual chlorine is to be measured. In the resulting chemical reaction, the total (free plus combined) residual chlorine oxidizes the iodide to iodine, as shown in the following example:

$$4I^- + HOC\ell + NH_2C\ell + 2H^+ \rightarrow 2I_2 + 2C\ell^- + NH_3 + H_2O. \quad (1)$$

The iodine in turn is reduced at a noble metal electrode producing current proportional to the concentration of iodine, and hence chlorine, in the original sample. Close control of sample and reagent flow is often required in these sensors.

3.3.1.3 In colorimetric sensors the sample is conditioned with an indicator chemical, e.g., N, N-diethyl-p-phenylene diamene (DPD), and with buffering and other reagents, e.g., potassium iodide for combined residual chlorine measurement. The colored solution passes through a calibrated photometer from which the corresponding residual chlorine can be determined. Corrections for background color and turbidity may be necessary and are sometimes accomplished internally within the instrument.

3.3.2 Amperometric and colorimetric sensors are used as flow-through devices; a sample is continuously withdrawn from the process and, after conditioning with reagents as necessary, is made to flow through the sensor. Polarographic sensors are separated from the sample by a membrane and in principle could be directly

immersed in the wastewater. However, if a buffer or other reagents are needed (as is often the case in wastewater) the sensor must operate outside of the wastewater in a flow-through mode.

4. GUIDELINES FOR SPECIFICATIONS

4.1 General Requirements.

4.1.1 On-line analyzers must be designed for continuous operation.

4.1.2 Analyzers furnished for use in wastewater treatment plants shall be capable of measuring total residual chlorine, with the exception of the case of paragraph 4.1.3.

4.1.3 When breakpoint chlorination is specified the analyzer must be capable of measuring free residual chlorine. In this case only the free residual should be measured, to the exclusion of the combined residual, so that the latter cannot be mistaken for free with resulting process failure. It is preferable that an analyzer system be convertible from total to free residual measurements, or vice versa, simply by changing reagents or sensing cells.

4.2 Range. The required range will depend upon the specific application. For example, an analyzer that samples water close to the point of chlorine injection clearly is subject to higher chlorine concentrations than one that is sampling final effluent. Typically, analyzers to be used in the contact tank should be capable of measuring residual to 10 mg/ℓ; however, note paragraph 4.3 1 regarding range selection. In this regard, portable monitoring instruments which may be used at several locations require greater flexibility than permanently installed on-line units; switch-selectable ranges are desirable here.

4.3 Performance Parameters.

4.3.1 Accuracy. The acceptable level of accuracy for analyzers used for effluent monitoring shall be within ± 3 percent of full scale. Because manufacturers frequently cite accuracy figures in this manner, i.e., in terms of full scale or measurement range, it is important to select as low a meter range as possible for the given application and to be aware of the absolute accuracy (e.g., 0.03 ppm for a 0-1 ppm instrument) associated with the cited accuracy. There may be applications for which a stricter accuracy specification is necessary.

4.3.2 Precision. The precision shall be within ± 1 percent of range, in order to minimize excursions during process control. It is noted that for most <u>control</u> applications, precision or repeatability may be more important than accuracy. However, for effluent <u>monitoring</u>, both accuracy and precision are important.

4.3.3 Sensitivity. The sensitivity shall be at least 0.01 mg/ℓ for either control or monitoring units.

4.3.4 Response time. An analyzer should register at least 90 percent of a step change within 3 minutes. Instruments with response times substantially less than this are commercially available and may be desirable in the interest of reducing loop time in control applications.

4.3.5 Drift. The drift of the analyzer following the initial stabilization period shall be within ± 1 percent of full scale for seven days when subjected to a constant residual-chlorine solution.

4.3.6 Temperature effects.

4.3.6.1 The amperometric signal for both polarographic and amperometric sensors is temperature dependent, with a coefficient of approximately 3 percent per degree C. Therefore, temperature compensation is necessary, and in the case of on-line control instruments it must be accomplished automatically as part of the analyzer output.

4.3.6.2 Those of the above analyzers which are not used for control (as well as portable analyzers) may omit automatic temperature compensation. However, the instrument must at least contain provision for temperature measurement and the manufacturer must provide a chart which displays corrections to allow residual chlorine to be calculated from the instrument reading. In this event, the need for this manual correction should be prominently displayed on the readout.

4.3.6.3 In both of the above cases the manufacturer must provide information on the limiting sample temperatures for which the output is (or can be) compensated. The manufacturer must also provide information on the limiting ambient temperatures for proper operation of the instruments, if these differ from the sample-temperature limits.

4.3.6.4 Manufacturers of colorimetric instruments must provide information on the sensitivity of the analyzers to changes in ambient and sample temperatures, along with limiting operating temperatures.

4.3.7 Sensor cells.

4.3.7.1 If the sensor is of a type which requires periodic replacement of electrodes, such replacement should be possible by users at the plant. Replacement electrodes should be readily available to the user. Similar comments pertain to replacement of membranes and electrolytes. The date of electrode replacement should be clearly noted so

that subsequent replacements can be anticipated.

4.3.7.2 Electrochemical sensors should incorporate adequate cleaning mechanisms to prevent continuous buildup of contaminants on the electrodes and consequent drift beyond an initial stabilization period. Alternatively, in the absence of such mechanism the manufacturer should recommend procedures for accomplishing the same end. The manufacturer should also furnish an estimate of the stabilization time needed for a new sensor or for a sensor with new electrodes; a three-day stabilization time is typical.

4.3.8 Material. All parts of the analyzer shall be constructed of materials which are resistant to corrosion and which will not affect the chlorine residual readings. The principal corrosive influence will be hydrochloric acid. See also paragraph 5.2.1.8.

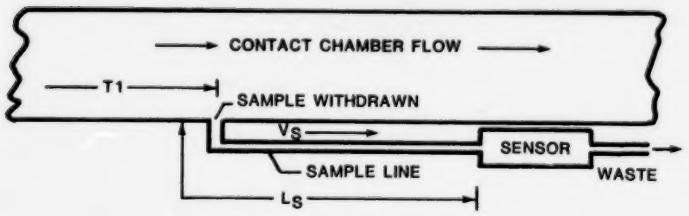
5. INSTALLATION

5.1 The installation of the analyzer and its stabilization must be in accordance with manufacturer's instructions, which shall be included in a user's manual.

5.2 Sampling System.

5.2.1 Flow-through sampling. An analyzer using flow-through sampling should have either a sampler that is an integral part of the instrument or an independent sampling system with its own pump or pressure line to provide adequate flowrate and appropriate velocity of sample flow to the analyzer as described in the following.

5.2.1.1 The contact time is equal to the time required for a volume element of liquid to go from the beginning of the contact tank to the point at which the sample is withdrawn, plus the time required to move through the sample line to the sensor. Thus, the velocity of sample flow and the length of the sampling line are to be chosen such that the arrival at the sensor of a volume element of sample corresponds to the desired contact time. This means, for example, that if the analyzer is located far from the contact tank, the sample may have to be withdrawn close to the injection point if it is to be representative of the contact-chamber effluent by the time it reaches the analyzer. See figure 1.



T1= CONTACT TIME UNTIL SAMPLE WITHDRAWAL

EFFECTIVE CONTACT TIME = $T1 + L_S / V_S$

Figure 1. Allowing for length of sample line.

5.2.1.2 The velocities selected in accordance with paragraph 5.2.1.1 are subject to the following additional constraints:

- The velocity must be maintained high enough to prevent deposition of suspended matter and to discourage slime formation in the line; and
- The velocity must not be so high as to break up suspended material and expose new surfaces to chlorine action.

- Velocities of about 1.5 m/sec (5 ft/sec) but no higher than 3 m/sec (10 ft/sec) will meet these constraints.

5.2.1.3 The foregoing requirements can be satisfied by selecting appropriate combinations of pump capacity and sample-line size.

5.2.1.4 Flowrate. The system must include means for the user to ascertain that the sample flowrate is within proper operating limits. If a flowmeter is necessary to satisfy this requirement, it shall be furnished by the manufacturer as an integral part of the equipment.

5.2.1.5 Sampling pump.

- If the sampling pump is not furnished as an integral part of the analyzer system, the manufacturer must provide the specifications necessary for its selection and installation.
- Pumps of the types which subject the sample to minimal shears (and suspended material breakup) are preferred. Positive displacement pumps are generally superior to centrifugal pumps in this regard.

5.2.1.6 Check samples. Provision must be made for withdrawal of a discrete check sample at the location where the sample enters the analyzer. This will enable one to calibrate or check the accuracy of the analyzer by an independent method.

5.2.1.7 Keeping sample lines clean.

- Filtering. Since effluents of wastewater treatment plants often contain suspended solids, some provision must be made to prevent constriction of the sampling system. Filtering at the inlet to the sampler is one possibility; where appropriate, the analyzer should also incorporate a fine filter or its equivalent ahead of the sensor cell. Users should be furnished guidelines for ascertaining, either visually or by other means, that analyzer filters need cleaning or replacement. See paragraph 7.2.2.1.

- Flushing. Provision shall be made (backflushing capability, convenient disconnection of sample line from the analyzer, or other means) for cleaning the sample line of deposits and coatings. As a related requirement, provision should be made to keep liquid flowing in the line at all times, even when the sensor is out of service. See paragraphs 6.1.3.2 and 7.2.2.4.

5.2.1.8 Materials. The sampling system should be constructed of materials which are corrosion resistant and will not affect readings by reaction with the residual chlorine.

5.2.2 Direct immersion sensors.

5.2.2.1 If the analyzer is of the type which uses a sensor immersed directly in the flow, the manufacturer must inform the user of any requirements concerning the velocity of the flow relative to the sensor.

5.2.2.2 If an agitator or other type of motion inducer is required, the manufacturer shall either make it available for purchase as part of the system or provide all information and specifications necessary for its procurement and installation.

5.3 Other requirements.

5.3.1 Reagent solutions.

5.3.1.1 If a chlorine analyzer requires addition of any reagent solutions, whether for the chlorine detection itself or for pH control, the reagent storage and delivery system must be furnished as an integral part of the analyzer.

5.3.1.2 The reagent storage should have sufficient capacity for reasonable length of operation under normally anticipated conditions. Twenty-four hours could be considered a minimum operating span for this purpose.

5.3.2 Readout and transmission.

5.3.2.1 An on-line analyzer shall have a readout at its own location as well as capability for transmission of the output to a central control room.

5.3.2.2 An on-line monitoring system, as part of its output, shall have the capability of activating an alarm to alert personnel to seriously high or low chlorine residuals.

5.3.2.3 The instrument shall have capability for manual adjustment of the zero and span readouts to allow for adjustment to reference levels during calibration.

5.3.2.4 The output shall be compatible with control devices and secondary devices, such as chart recorders, common to the industry.

5.3.3 Electrical. Electrically, the monitoring system as well as individual components shall meet all code requirements for the particular area classification.

5.3.4 Location.

5.3.4.1 It is preferable that the analyzer be located as close as possible to the sampling point, consistent with the consideration of paragraphs 5.2.1.1 and 5.2.1.2.

5.3.4.2 The analyzer must be protected from the elements and from temperature extremes.

6. MEASUREMENT ASSURANCE

6.1 Sampling.

6.1.1 The sampling procedure should ensure that the residual chlorine in the sample as it reaches the analyzer is representative of the average value in the chlorine contact tank after a specific time. This means that, at the point of withdrawal, the sample must be representative of conditions in the corresponding sectional plane of the contact tank, as described in section 6.1.2. It further requires an accounting of possible changes in the sample as it proceeds through the sample line; this is described in sections 6.1.3 and 6.1.4. Users are referred also to ASTM D-3370 (reference 8.3).

6.1.2 Representative samples.

6.1.2.1 If the injected chlorine has been well mixed with the effluent stream and if an essentially plug flow prevails in the contact tank, the chlorine concentration will be uniform at a cross-section and a sample will be representative of the sectional plane at which it is withdrawn. However, the existence of these conditions should be verified by checking the constancy of numerous residual chlorine measurements made across the sampling plane of the contact tank using a portable analyzer. (Note that for this application the repeatability of the analyzer is more important than accuracy).

6.1.2.2 As an alternate to the use of a portable analyzer, samples may be withdrawn from these points for measurement with an amperometric titrator, provided that the flow (wastewater and chlorine) is constant during the period when all samples are drawn and the time between the taking of each sample and its measurement is the same.

6.1.2.3 These measurements should be made for a high plant flow and a low plant flow. They may be waived if it can be established, from hydrodynamic principles or by other means, to the satisfaction of the involved parties that complete lateral mixing has been achieved.

6.1.2.4 Section 6.1.2 applies to both flow-through and direct-immersion sensors.

6.1.3 Sample integrity.

6.1.3.1 Resistance of the sample to mechanical degradation is enhanced by following the sample-line and pump recommendations of paragraphs 5.2.1.2 and 5.2.1.5.

6.1.3.2 The sample can also be affected by organic growth on the inside walls of the sample line, which could result in systematically low residual chlorine readings. This effect can be particularly important in long sample lines or in lines following dechlorination.

6.1.3.3 It is recommended that as soon as the analyzer is placed in service, the integrity of the sample against mechanical degradation be checked by comparing the residual chlorine concentrations of samples withdrawn from the contact tank at the intake to the sample line with samples taken from the sample line at the entrance to the analyzer (paragraph 5.2.1.6).

- Equivalence of the measurements indicates an absence of degradation.
- In long sample lines, the effect of additional contact time must be taken into account. See section 6.1.4.
- Repetition of these measurements periodically thereafter will reveal the onset of effects of organic growth and will help to provide a basis for establishing a flushing frequency for sample-line maintenance (paragraph 6.1.4.3). The frequency of this repetition depends upon the operating condition of the plant. A weekly check is recommended initially; the frequency can be reduced as experience warrants.

6.1.3.4 Section 6.1.3 does not apply to direct-immersion sensors.

6.1.4 Characterizing the residual chlorine decay curve.

6.1.4.1 When measured residual chlorine concentration is plotted against contact time, the resulting curves usually display a relatively rapid drop for the first few minutes with a gradual exponential decay thereafter. See figure 2. It is important that the approximate shape of these curves be known so that the effects of contact time on a sample can be taken into account if necessary.

6.1.4.2 After plant startup, but prior to activation of the residual chlorine analyzers, make residual chlorine measurements with a portable analyzer at points along the contact basin corresponding to a range of post-injection times; for example, from five to 60 minutes.

- Enough repetitions of this survey should be made to yield the residual chlorine decay curve (figure 2) or curves that are characteristic of the basin.

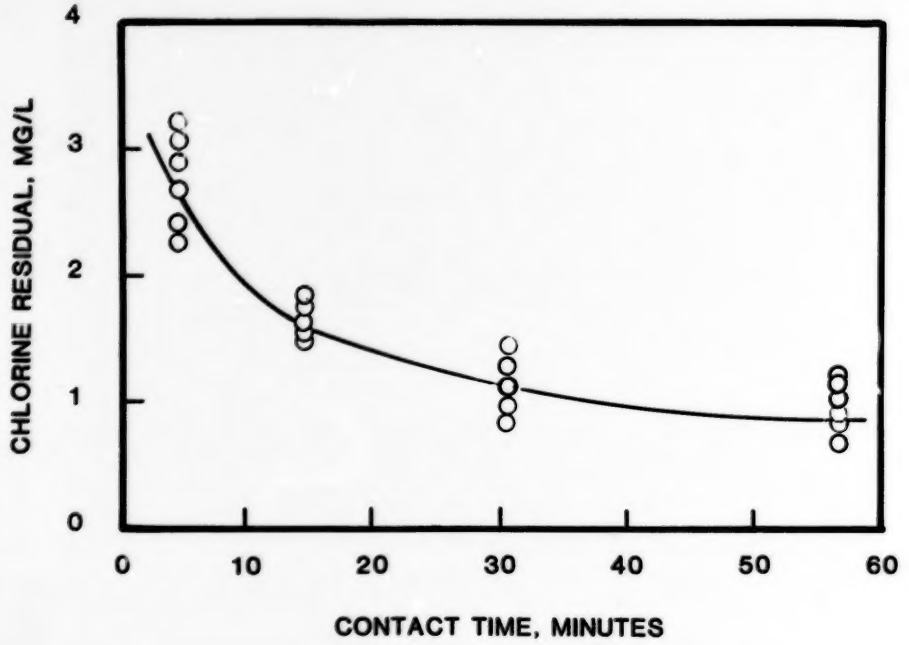


Figure 2. Typical variation of residual chlorine with contact time.

- This survey can also be made by performing measurements on grab samples. In that event, the time elapsed between sample withdrawal and titration should be taken into account in plotting figure 2.

6.1.4.3 Use the residual chlorine decay curves (figure 2) as a basis for checking the condition of the sample line in paragraph 6.1.3.3. If the residual chlorine loss in the sample line is greater than the reduction during the corresponding contact time, it is likely that the sampling line requires cleaning.

6.1.4.4 Subsequent to the initial determination of the decay curves (figure 2), periodic check measurements should be made in the contact tank to confirm their continued applicability. The frequency of these measurements must be established by experience.

6.2 Calibration.

6.2.1 General. For accurate performance, all measuring instruments require calibration. In principle, residual chlorine analyzers could be calibrated in the following ways:
- On an absolute basis using coulometry and electrochemical principles;

- By measuring a sample of unknown chlorine concentration with both the analyzer to be calibrated and a reference analyzer, i.e., a transfer standard;
- By comparing the analyzer output with the results of a "standard" chemical analysis of the same sample. This is the method generally used in wastewater treatment plants.

6.2.2 Reference measurements.

6.2.2.1 Analyzers shall be calibrated against the iodometric back-titration method, preferably using amperometric end-point detection. The absence of interferences shall be checked by spiking a reference solution of known concentration into plant wastewater. For analyzers that incorporate internal absolute coulometric calibration, a procedure should be developed for assuring the performance of the calibration cell; this may include periodic comparisons with titration calibrations.

6.2.2.2 The laboratory procedures and related instructions cited in reference 8.1 or 8.2 (or equivalent publications) shall be followed.

6.2.2.3 Since the chlorine concentration in the sample tends to decay gradually, titrations should be made as soon as possible after the sample is drawn. Decay corrections must be made as necessary.
- Refer to the decay curve of section 6.1.4 to check that the elapsed time between sample withdrawal and analysis either is short enough to have insignificant effect on the results or is otherwise accounted for.
- Always keep samples away from direct sunlight. Sample bottles should be made of brown glass or should be provided with an external covering.

6.2.2.4 If a commercial amperometric titrator is used, all procedures and maintenance instructions given in the user's manual shall be followed.

6.2.2.5 A reference measurement other than that of paragraph 6.2.2.1 can be used in certain circumstances where the following conditions are met:
- The proposed reference method is well-documented in the literature in regard to precise procedures, reagents, interferences, accuracy, etc., or equivalent information can be otherwise established to the satisfaction of involved parties.
- It can be shown to the satisfaction of involved parties that the method used is adequate for the particular plant effluent.

6.2.3 Calibration procedure.

6.2.3.1 This section applies to both on-line and portable analyzers.

6.2.3.2 Calibration of an analyzer shall incorporate any specific instructions detailed by the manufacturer in the operator's manual.

6.2.3.3 A new analyzer should be calibrated before it is placed in service at a minimum of three concentrations (zero, medium and high) within its anticipated range.

- The use of three points enables the user to check the basic linearity of the instrument. If the response is linear, subsequent checks need only include the zero and high points unless substantial changes are made in the sensor or become evident in the output.
- The "medium" and "high" concentrations can be obtained by moving the sample intake or the sensor to points in the contact tank having appropriate contact times as shown in figure 2. Start with the high concentration.
- The "zero" condition can generally be obtained for each instrument in an off-line mode from manfacturer's instructions. Use this condition to adjust the readout to zero.
- In regard to initial calibrations, an instrument which has undergone a change of electrodes and/or electrolyte should be treated as a new instrument. In both cases, the recommended stabilization period should be allowed before calibration measurements are started.

6.2.3.4 For each concentration being calibrated, select a time when plant flow, chlorine flow and other conditions appear to be constant. Withdraw a sample from the tap provided in paragraph 5.2.1.6 (or from the tank next to an immersed sensor), measure it immediately and compare the result with the analyzer reading made when the sample was drawn. The following should also be done:

- If necessary, correct the titration result for elapsed time per paragraph 6.2.2.3.
- Enter the point so obtained on a plot in which the ordinate is the analyzer readout in mg/ℓ and the abscissa is the titration result in mg/ℓ. See figure 3 as an example. On such a plot a 45-degree line through the origin represents the condition of equivalence.
- Spiking the natural sample may be necessary to speed up the calibration. This involves adding a known amount of chlorine to the sample and measuring both the spiked and unspiked concentrations; the difference should be equal to the added chlorine.

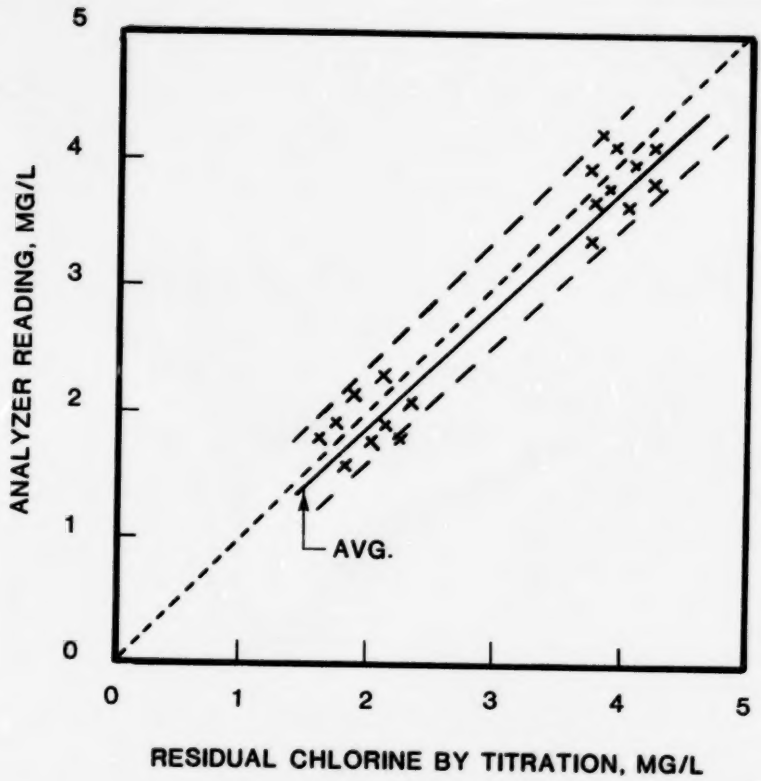


Figure 3. Calibration check.

- It is recommended that the readout span not be adjusted, i.e., the instrument not be calibrated, based on this one point, but rather that a cluster of several points be obtained in rapid succession at (ostensibly) the same concentration (paragraph 6.2.3.5).

6.2.3.5 Repeat the pair of readings, as indicated in the preceding paragraph, from six to ten times at both the medium and high concentrations and plot the points, as on figure 3.

- Draw a curve (which should be essentially a straight line) through the average of the point clusters either visually or by calculated averages as necessary.
- If the line so drawn deviates from the 45-degree line by more than the accuracy limit of section 4.3.1, the span adjustment can be used to calibrate the analyzer. (This procedure assumes that the reference method which has been accepted as a standard is completely accurate, i.e., is a "true" value. By mutual agreement, the involved parties may wish to assign an uncertainty to the reference measurement. Should this be the case, the analyzer could deviate from the 45-degree line by an amount equal to the allowed inaccuracy plus the assigned uncertainty.)
- The horizontal scatter of the cluster of points at a given concentration (figure 3) is indicative of the precision of the reference measurements plus any unavoidable changes in the actual concentration as the successive samples are withdrawn. The vertical deviations around the average are an indication of the precision of the analyzer and should not exceed the specified value (section 4.3.2) plus an allowance for the estimated precision of the reference measurements.

6.2.4 Calibration frequency.

6.2.4.1 During the period immediately following the initial calibration described in section 6.2.3, the analyzer should be monitored by comparing its readings with sample titrations several times daily.
- A boundary of uncertainty should be established for each analyzer installation and method of measuring reference concentration. This can be a multiple of standard deviation, a percent of indicated value, a percent of the full scale value, or a specific concentration value. This is an arbitrary value selected by experience with the analyzer and reference methods and mitigated by the absolute accuracy required for the specific application. The limits are drawn (dashed lines) symmetrically about the average line as shown, Figure 3.
- When the monitoring points begin to drift consistently outside of these limits in either direction, it may be time to reset the calibration (zero and span) and/or do routine sensor cleaning.

6.2.4.2 Continuation of the relatively intensive monitoring of paragraph 6.2.4.1 for a period of at least two weeks after the analyzer is placed in service will furnish data which will help develop a recommended calibration schedule for routine operations. Typically, this re-

calibration schedule is between once daily and once weekly. See paragraph 6.2.3.3 for requirements on routine recalibrations and on recalibrations of refurbished sensors.

7. MAINTENANCE

7.1 Long Term.

7.1.1 Manufacturers shall provide recommendations for long-term maintenance in the user's manuals accompanying the instruments.

7.1.2 As a general practice, the complete residual chlorine monitoring system should be serviced on a quarterly basis. This service should include all components of the monitoring loop, i.e., sampling system, measurement cell, especially the electrodes and channels, buffer and reagent delivery systems, transmitter, recorder, and alarm systems. This service should include cleaning of all pertinent components, repair and replacement of malfunctioning parts, reassembly and final recalibration of the entire system.

7.1.3 It has been reported that monitors used with dechlorinated effluent tend to become subject to drift problems after extended periods in water with essentially zero residual chlorine. As a precautionary measure, performance should be checked periodically to detect the onset of this behavior. Consideration should be given to periodically alternating the effluent analyzer with a control analyzer further upstream in the process, i.e., in the chlorine contact tank. As an alternative to alternating analyzers, two electrodes can be made available for each analyzer, with one of each pair being stored in a chlorine solution for conditioning. They can be switched on a regular basis or when drifting is detected. A further alternative would be to periodically add a spike solution to the sample to shock the analyzer and simultaneously check its response and accuracy.

7.2 Short Term.

7.2.1 Manufacturer shall provide recommendations for short-term maintenance in the user's manuals accompanying the instruments.

7.2.2 As a supplement to manufacturers' guidelines, the following procedures are recommended.

7.2.2.1 Check and if necessary clean filters daily.

7.2.2.2 Check the sample flow daily.

7.2.2.3 Check the reagent flows daily.

7.2.2.4 Purge or reverse flush the sample line periodically, at intervals (typically weekly) determined in part by the tests described in section 6.1.4. It is noted in this regard, that sample lines used in dechlorination are likely to contain little or no residual chlorine and are thus particularly susceptible to sliming. One possible procedure is to disconnect the sample line from the analyzer and flush the line with a biocide.

7.2.2.5 Flush flow-through sensors weekly or as indicated in paragraph 6.2.4.1.

7.2.2.6 Check the sample pH (downstream of the addition of the buffering) daily to determine whether it is within prescribed limits.

7.2.2.7 In direct-immersion sensors, wipe the membrane clean daily.

8. REFERENCES

8.1 American Public Health Assoc., "Standard Methods for the Examination of Waste and Wastewater," 14th ed., 1975.

8.2 ASTM, "Standard Test Methods for Residual Chlorine in Wastewater," D1427-68 (Reapproved 1974).

8.3 ASTM, "Standard Practices for Sampling Water," D3370-76.

8.4 Water Pollution Control Federation, "Chlorination of Wastewater," WPCF Manual of Practice No. 4, 1976.